

Aqueous processed Li-ion battery electrodes with hydrolyzed polyacrylonitrile binder

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1. Experimental details

Materials

Hydrolyzed polyacrylonitrile (HyPAN, Burkhimsnab, Russia), $M_w = 3 \times 10^5$, contained acrylic acid and acrylamide monomer units in a molar ratio of 75:25^{S1} and was purified by reprecipitation. For this purpose, 4 g of HyPAN was dissolved in 200 mL of distilled water; 5 mL of 10 M HCl was added to the prepared solution on a magnetic stirrer. After stirring for 1 h, the precipitate formed was filtered off, washed with distilled water, and dried at 60 °C. The resulting protonated HyPAN was suspended in distilled water (20 mg mL⁻¹), then aqueous solution of LiOH (75 mg mL⁻¹) was added dropwise until HyPAN was dissolved and pH reached 5.

Polyvinylidene fluoride SolefTM 5130 (PVDF, Solvay S.A., Belgium), carboxymethylcellulose (CMC, Gelon LIB, China), aqueous dispersion of styrene-butadiene rubber (SBR, Gelon LIB, China), carbon-coated LiFePO₄ (BTR, China), and single-walled carbon nanotubes TuballTM (SWCNTs, “Tuball”, OCSiAl, Russia) were used as received. Double distilled water and *N*-methyl-2-pyrrolidone (Khimmed, Russia) were used as solvents to prepare electrode slurries.

Preparation of the electrodes

Solutions of the polymer binders (20 mg mL⁻¹) were prepared. HyPAN and CMC/SBR (CMC:SBR = 1:1 w/w) were dissolved in water, whereas PVDF was dissolved in NMP. SWCNTs were dispersed in the binder solutions (1.05 mg mL⁻¹) for 10 min by tip-ultrasonication using a Vibra-Cell VCX 750 ultrasonic processor. The resulting dispersions were thoroughly mixed with LiFePO₄ powder; the fraction of LiFePO₄ was 95 wt.% with respect to the total solids content. The resulting slurries were spread on the surface of carbon-coated aluminum foil current collector (Gelon LIB, China) using a doctor blade applicator (Novotest AU-823) with a 300 µm gap. After being dried in air for 1 day, the coatings were roll-pressed. The disc-shaped electrodes (2 cm² area) were cut out of the resulting laminates, weighed with 0.01 mg accuracy, and after that dried under dynamic vacuum at 110 °C for 4 h. The active mass loading of LiFePO₄ was *ca.* 4 mg cm⁻².

Characterization

To determine the SWCNTs dispersion yield, the SWCNTs-HyPAN dispersions were centrifuged at 12000 rpm for 10 min. After the precipitate was removed, the concentration of SWCNTs in the remaining dispersion was determined by electron spectroscopy using a preliminary determined extinction coefficient of $38.7 \text{ mL mg}^{-1} \text{ cm}^{-1}$ at 500 nm (Figure S4).

Scanning electron microscopy (SEM) images of the electrodes were obtained using a Helios G4 PFIB UXe DualBeam microscope (ThermoFischer Scientific, Waltham, MA, USA)

The electrodes were tested in electrochemical half-cells with lithium metal foil anode, Celgard 2500 microporous polypropylene separator and 1M $\text{LiPF}_6/\text{EC}:\text{DMC}$ (1:1 v/v) electrolyte (Sigma Aldrich). The potentiostatic charge/discharge experiments were performed using a P-20X8 potentiostat-galvanostat (Electrochemical Instruments, Russia) within the potential range of 2.0–4.0 V vs. Li/Li^+ . The capacity values were normalized by the weight of LiFePO_4 material. Cyclic voltammetry characterization was carried out at the scan rate of $100 \mu\text{V s}^{-1}$.

2. Electrochemical stability of HyPAN binder

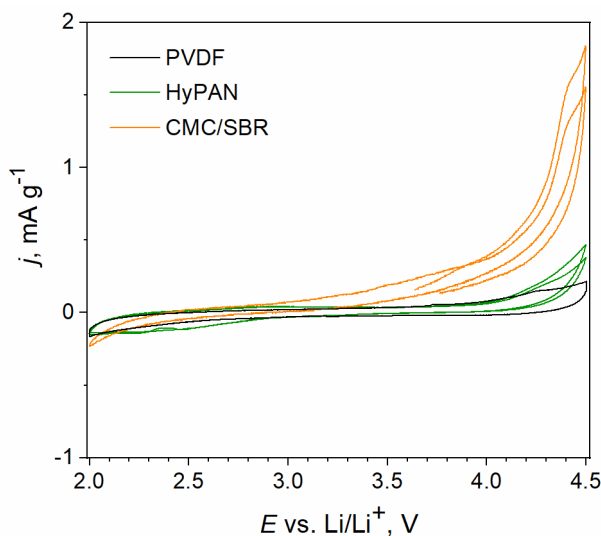


Figure S1 Cyclic voltammograms of the binder films ($100 \mu\text{V s}^{-1}$).

3. Dispersibility of SWCNTs in HyPAN solutions

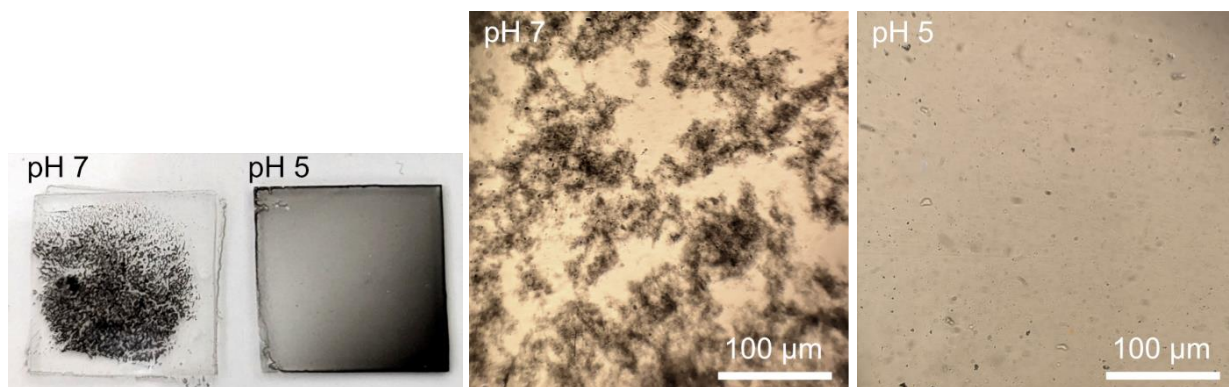


Figure S2 Optical images of the SWCNTs dispersions in HyPAN aqueous solutions at different pH (1.05 mg mL^{-1} of SWCNTs, 20 mg mL^{-1} of HyPAN).

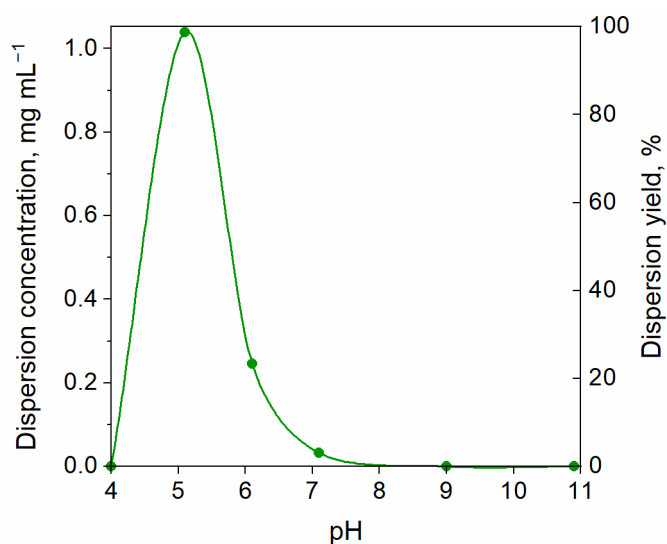


Figure S3 Dispersibility of SWCNT in the aqueous HyPAN solutions as a function of pH.

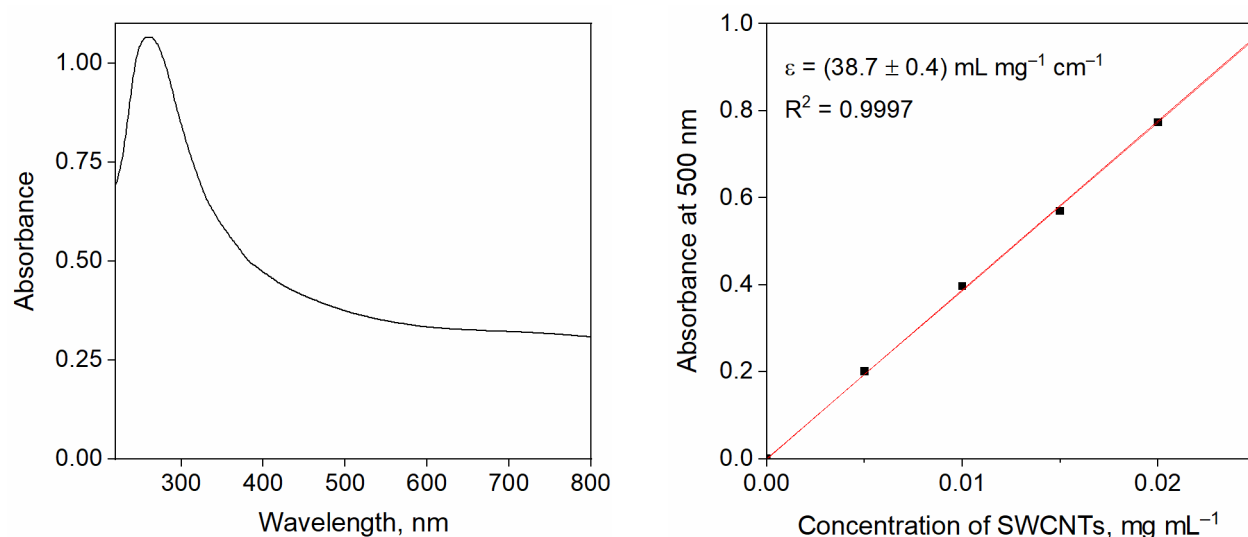


Figure S4 UV-vis. spectrum of SWCNT (0.39 mg mL⁻¹) in the aqueous HyPAN solution and the determination of extinction coefficient at 500 nm.

4. Galvanostatic profiles of the LiFePO₄-based electrodes prepared with different binders

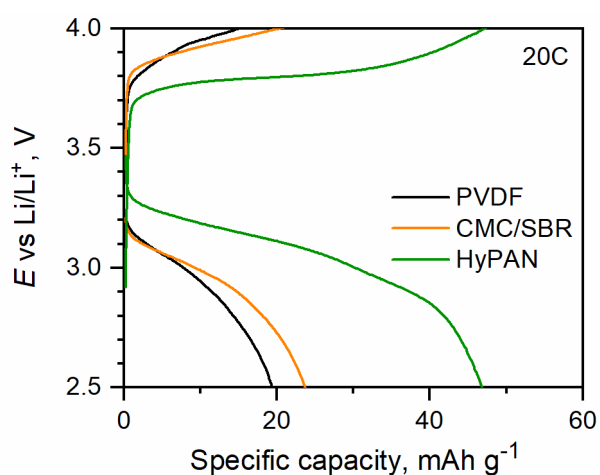


Figure S5 Galvanostatic profiles of the composite electrodes prepared with different polymer binders at 20C charge-discharge rate.

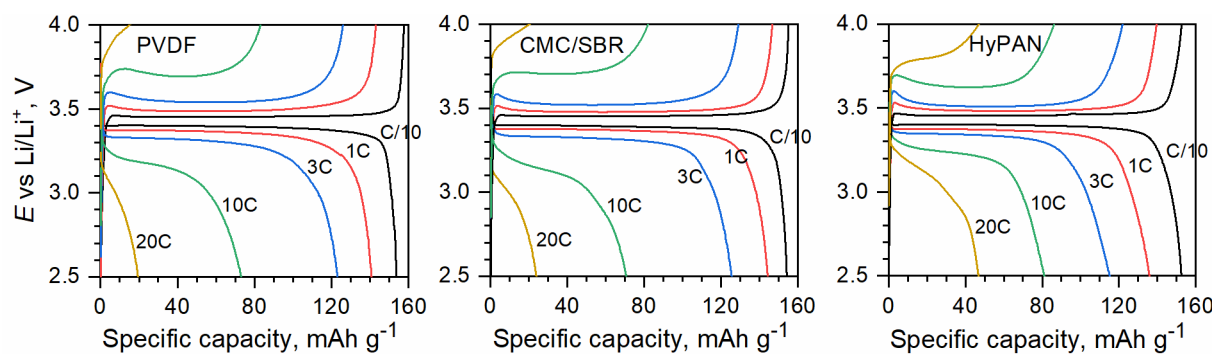


Figure S6 Galvanostatic charge-discharge curves of the composite electrodes prepared with different polymer binders.

Reference

- S1 A. V. Kubarkov, A. A. Asharchuk, O. A. Drozhzhin, E. A. Karpushkin, K. J. Stevenson, E. V. Antipov and V. G. Sergeyev, *ACS Appl. Energy Mater.*, 2021, **4**, 12310;
<https://doi.org/10.1021/acsaem.1c02135>.